Supporting Information

In-Situ Exfoliation of Graphene in Epoxy Resins: a Facile Strategy to Efficient and Large Scale Graphene Nanocomposites

Yan Li [1], Han Zhang [1,2], Maria Crespo [1], Harshit Porwal [1,2], Olivier Picot [1,2], Giovanni Santagiuliana [1], Zhaohui Huang [3], Ettore Barbieri [1,2], Nicola M. Pugno [4,5,1], Ton Peijs [1,2], Emiliano Bilotti [1,2*]*

[1] School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, E1 4NS, London, UK

[2] Nanoforce Technology Ltd., Mile End Road, E1 4NS London, UK

[3] School of Materials Science and Technology, China University of Geosciences , 100083, P. R. China

[4] Laboratory of Bio-inspired & Graphene Nanomechanics, Department of Civil, Environmental and Mechanical Engineering, University of Trento, Via Mesiano 77, 38123 Trento, Italy

[5] Center for Materials and Microsystems, Fondazione Bruno Kessler, Via Sommarive 18, 38123 Povo, TN, Italy

*Email: e.bilotti@qmul.ac.uk (Emiliano Bilotti), t.peijs@qmul.ac.uk (Ton Peijs)

Content

Modelling of the TRL calendaring process

Rheology of epoxy resin

Surface tension

Morphology of particles

Review of graphitic nanoparticles and their composites properties

Summary of processing parameters

Reference

Modelling of the TRM calendaring process

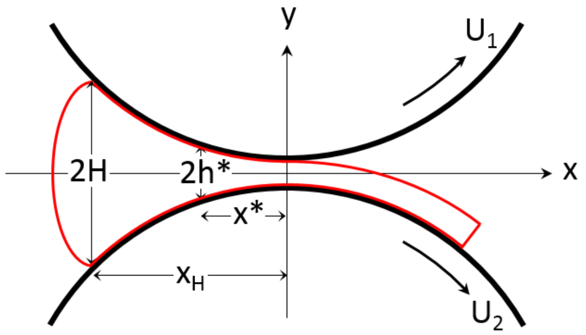

Figure S1. Schematic of nip region between two counter rotating rolls in the TRM Process.

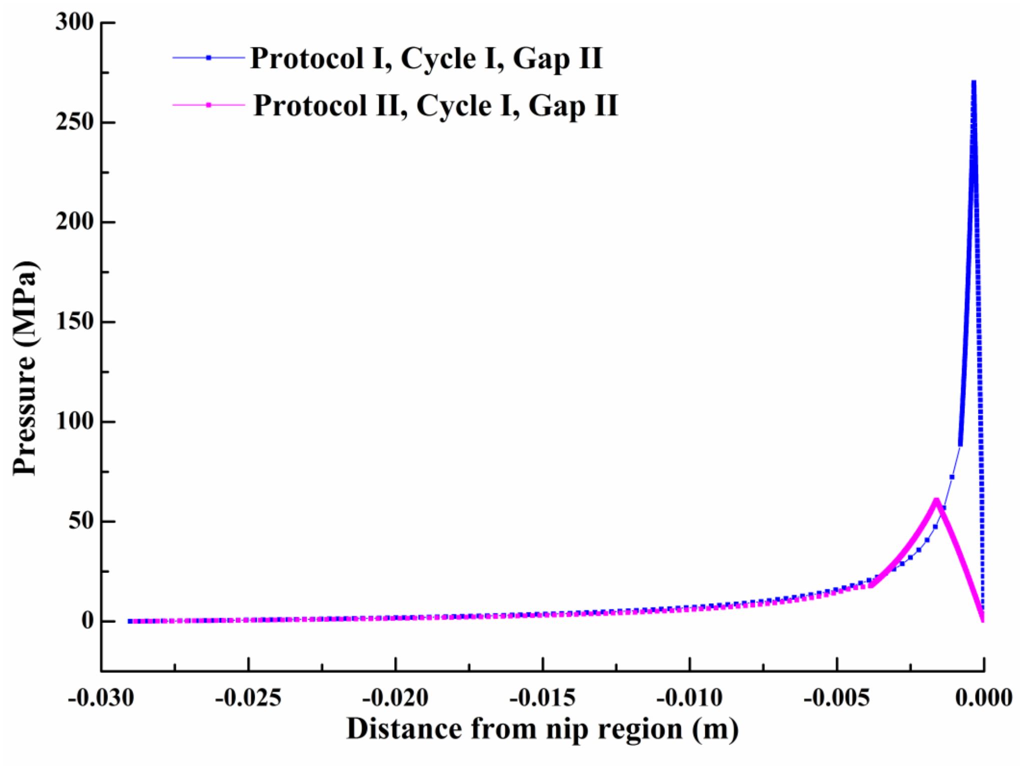

Figure S2. Pressure profile in TRM for Protocol I and II, for Cycle I, Gap II. The pressure assumes a maximum for $x=x^*$ and $h=h^*$. It is noted that the ratio h^*/h_0 is found to vary within a narrow range of values (1.5-1.6) for all processing conditions evaluated and modelled.

Rheology of epoxy resin

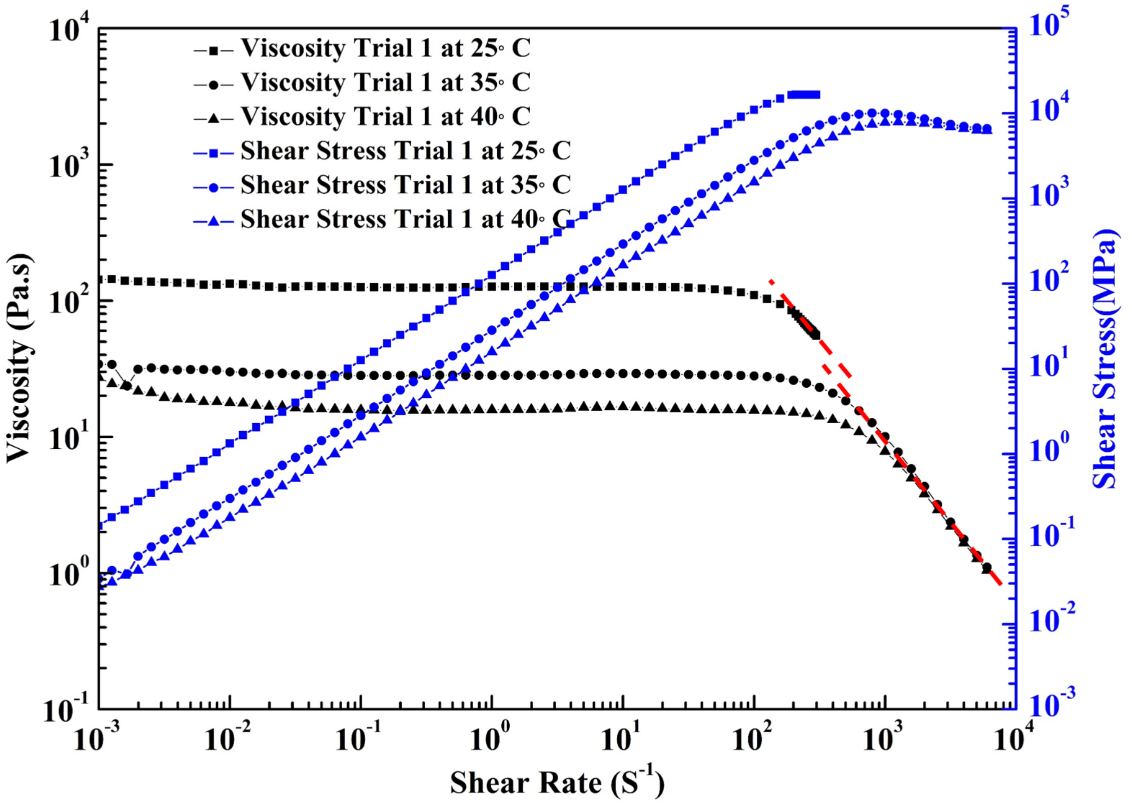

Figure S3. Viscosity and shear stress of pure epoxy as function of shear rate, at 25, 35, 40° C.

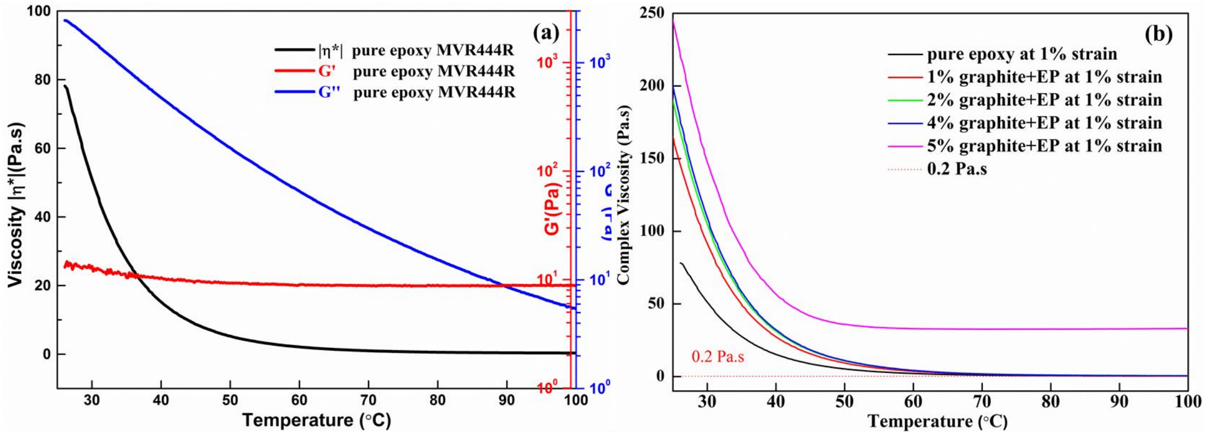

Figure S4. (a) Viscosity of the epoxy and hardener as a function of temperature. (b) Viscosity of epoxy resin filled with various loadings of graphite as a function of temperature.

Surface tension

Drop shape analyser was used to measure the interfacial tension between the liquid epoxy and glass substrate. Surface energies were calculated from contact angle data of sessile drops. Base line and sessile droplet fitting were included for comparison. The most complicated, but also the theoretically most exact method for calculating the contact angle is the Young-Laplace equation [1, 2]. A given system of solid, liquid, and gas at a given temperature and pressure has a unique equilibrium contact angle. Indices S, L and G stand for "solid", "liquid" and "gas"; the symbols γ_{SG} and γ_{LG} describe the surface tension of two phases (solid-liquid and liquid-gas, respectively); and θ stands for the contact angle, corresponding to the angle between vectors γ_{LG} and γ_{SL}.

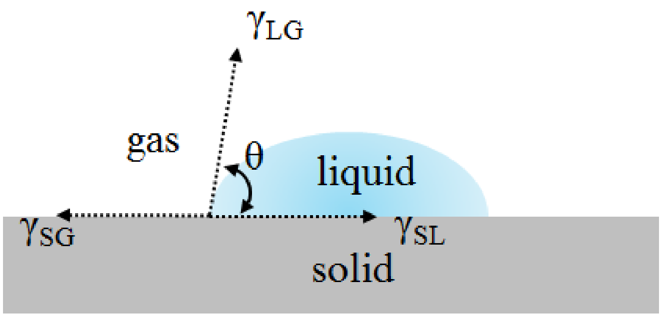

Figure S5. Schematic of a liquid drop showing the quantities according to the Young's equation.

The shape of a liquid/gas interface is determined by the Young-Laplace equation, with the contact angle playing the role of a boundary condition via Young's equation:

$$\gamma_{SG} = \gamma_{SL} + \cos\theta * \gamma_{LG} \tag{1}$$

During the experiment, we use the same glass substrate to keep the same surface roughness, and try to avoid potential contamination, or influence of possibly varying ambient conditions. In this method the complete drop contour is evaluated; the contour fitting includes a correction which takes into account the fact that it is not just interfacial effects which produce the drop shape, but that the drop is also distorted by the weight of the liquid it contains. After the successful fitting of the Young-Laplace Equation the contact angle is determined as the slope of the contour line at the three phases contact point. However, the calculation is only reliable for contact angles above 30°. Moreover, this model assumes a symmetric drop shape.

In order to make experiments easier, we choose a solvent, ethylene glycol, as a reference, whose surface tension is 47.70 N/m at 20 °C, with the boiling point at 197.3 °C (difficult to evaporate at 20 °C during the experiment procedure). Several μl ethylene glycol can maintain a good axisymmetric droplet profile on the glass substrate. With the measured volume, contact angle, the interfacial tension between the droplet and glass substrate can be calculated. According to Equation (1), the equilibrium condition can be described as follows,

$$\gamma_{Glass} = \gamma_{IFT1(\text{Glass,Ethylene glycol})} + \cos\theta_1 * \gamma_{Ethylene\ glycol} \tag{2}$$

$$\gamma_{Glass} = \gamma_{IFT2(\text{Glass,Epoxy})} + \cos\theta_2 * \gamma_{Epoxy} \tag{3}$$

Where, γ_{Glass}, $\gamma_{Ethylene\ glycol}$, γ_{Epoxy} represent the surface tension of the glass substrate, ethylene glycol and epoxy resin MVR444R, respectively. $\gamma_{IFT1(\text{Glass,Ethylene glycol})}$ and $\gamma_{IFT2(\text{Glass,Epoxy})}$ respectively, represent the interfacial tension of the ethylene glycol droplet and epoxy resin MVR444R with the glass substrate. θ_1 and θ_2 are the contact angles of ethylene glycol and epoxy resin with glass substrate under equilibrium condition. The surface tension of epoxy resin MVR444R is calculated as follows,

$$\gamma_{Epoxy} = \frac{(\gamma_{IFT1} - \gamma_{IFT2}) + \cos\theta_1 * \gamma_{Ethylene\ glycol}}{\cos\theta_2}, \qquad \gamma_{Epoxy} = \frac{(\gamma_{IFT1} - \gamma_{IFT2}) + 47.7 * \cos\theta_1}{\cos\theta_2} \tag{4}$$

Morphology of particle

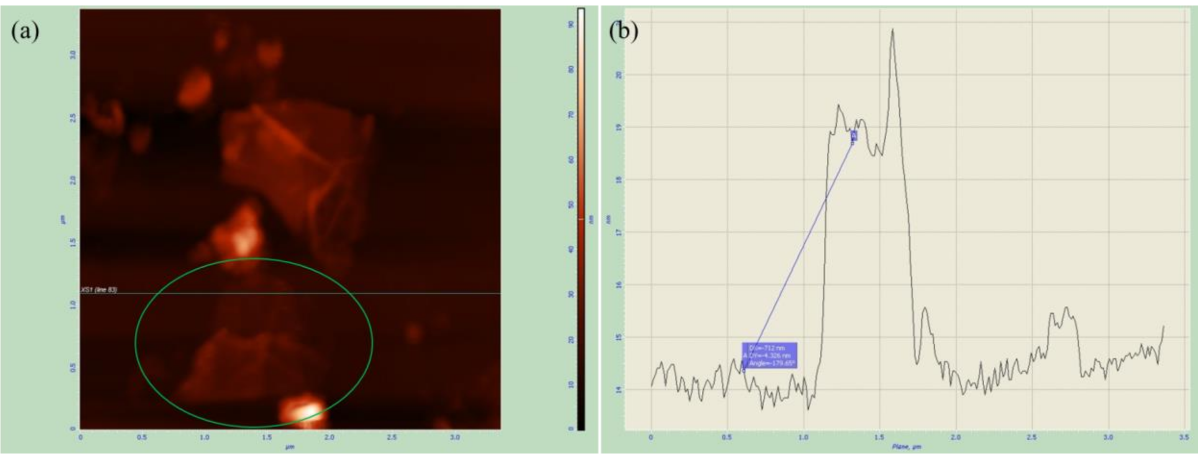

Figure S6. (a) Semicontact mode AFM image of GNP particle obtained from Procotol III (35 °C). (b) Thickness measurement of the obtained GNP particle obtained from Procotol III (35 °C) (thickness t = 4.326 nm).

Review of graphitic nanoparticles and their composites properties

Table S1. A summary of the sizes of GNPs reported so far in scientific literature.

Matrix/Substrate	Carbon source	After Exfoliation Particle Dimension	Fabrication of the Filler	Ref
NMP	Graphite flakes	6-12 layers, ~ 1.0-3.5 µm	Bath /Probe sonication	3
NMP	Graphite powder	63 mg/mL, 3 layers, ~1.0* 0.5 µm	Bath sonication/Probe sonication	4
90 wt.% water/[BMIm]Cl electrolyte	Graphite	Carbon nanoribbons (10 nm* (60 ± 20) nm) In water-rich ILs, the size of the carbon nanoparticles is larger (8-10 nm); In pure ILs, carbon nanoparticles are 2-4 nm.	Ionic liquid-assisted electrochemical exfoliation	5
Ni film on a SiO_2/Si substrate	Methane -CH_4	1 to ~12 graphene layers.	CVD on polycrystalline Ni films	6
DMF	Expanded graphite (EG)	Yield of 4–5 wt.% , thickness of graphene layer, decreases from 6–7 nm to 0.75–1.07 nm	Ultra sonication and centrifugation	7
DMF	Highly oriented pyrolytic graphite (HOPG)	Lateral size ~ several hundred nm, thickness: several nm, low yield	Bath sonication and centrifugation	8
potassium permanganate, sodium nitrate, and sulfuric acid	HOPG	Lateral size ~ 10 µm, 100% monolayer , thickness 0.96 nm	Chemical exfoliation by Hummers method	8
H_2SO_4 solution	HOPG	Lateral size ~ 1.0-2.0 µm, thickness 2.1 nm	Electrochemical expansion and exfoliation	8
Ionic liquid and water as electrolyte,	Graphite Rod	Several hundred nm, thickness: 1.1 nm	Electrochemical exfoliation	9
$LiClO_4$ and proprylene carbonate as electrolyte, -15 ± 5 V	Graphite powder or HOPG	Thickness 1.5 nm, lateral size 1-2 µm	Electrochemical exfoliation assisted by >10 h	10

			sonication	
0.48 g/L H_2SO_4 applying DC bias from -10 V to +10 V	Natural graphite flakes or HOPG	Thickness 1.5 nm, lateral size several µm	Electrochemical exfoliation	11
0.1 MSDS aqueous solution, 12 h from -1 V to 2 V.	Graphite Rod	Thickness 1.0 nm, lateral size ~ several hundred nm	Electrochemical exfoliation	12
1 M $HClO_4$ solution, 20 min from -1.6 V to 2 V	Laminated graphite foil	Lateral size several µm	Electrochemical exfoliation	13
Potassium permanganate, sodium nitrate, and sulfuric acid	Natural graphite flakes	Thickness 1.2 nm, lateral size ~ several hundred µm	Chemical exfoliation by Hummers method	14
Potassium permanganate, sodium nitrate, and sulfuric acid	Natural graphite particles or HOPG	Thickness 0.93 nm, lateral size 10-20 µm	Chemical exfoliation by Hummers method	15
Potassium permanganate, sodium nitrate, and sulfuric acid	Acid intercalation graphite flakes	Thickness 0.94 nm, lateral size 11-14 µm	Chemical exfoliation by Hummers method, microwave assisted expansion	16
NMP	Graphite powder	Thickness 3 layers, lateral size : several hundred nm, 4.0 wt.% monolayer	Bath sonication.	17
2 wt.% sodium cholate aqueous solution	Graphite flakes	thickness 1-2 nm, lateral size 100 nm	Horn sonication	18
Water with 2 wt.% surfactant Sodium dodecylbenzene sulfonate (SDBS)	Graphite powder	>40% of these flakes had <5 layers, ~3% of flakes consisting of monolayers, thickness 1 nm, lateral size 250 nm	Bath sonication	19
Organic solvents such as N-methyl-pyrrolidone	Graphite	1 wt.% monolayer	Bath sonication	20
Water/acetone mixtures	Graphite	0.21 mg/ ml ~50% of the nanosheets < 1 nm thick	Mild sonication for 12 h	21
DMF	Multi-layered graphite nanosheets	0.8-1.8 nm	Wet ball milling	22

A variety of organic solvents	Graphite nanosheets	Thickness 0.8~1.8 nm, lateral size 100–200 nm	Ball-milling	23
Polystyrene	Graphite nanoplatelets	Mono- and few-layer graphene, ~ 1.74 nm	Ball-milling	24
PVC dispersed in dioctyl phthalate DOP (adhesive)	Natural graphite	1.13-1.41 nm	Three Roll Mill	25
silicone polymer	Graphite nanoplatelets	Thickness ~ 5 to 35 nm	Three Roll Mill	26
Sylgard184SiliconeElastomer	graphite nanoplatelets	Thickness 20-200 nm, lateral size 5 μm	Dual asymmetric centrifuge mixing, Speed Mixer	27

Table S2. A summary of the sizes of GNPs reported so far in commercial market.

Graphene producer	**Graphene product**	**Details/Quality**	
Graphene Platform	Silver coated graphene	Silver Decorated Graphene with 30 wt.% , Particle size : 4.5 μm	
		Silver Decorated Graphene with 70 wt.% , Particle size : 7.2 μm	
	3D graphene	Grown on Cu/Ni Foam, continuous layer with few small multilayer islands coverage exceeding 95%.	
	Graphene dispersion	in NMP with non-ionic dispersant in NMP no surfactant	Different concentration 0.1,1.0,10,50,100 mg/ml, Purity : >99%, 1~10 Layers : >70%, >30 Layers : <5%
		in water with non-ionic dispersant	Different concentration 0.1,1.0,10 mg/ml, Purity : >99%, 1~10 Layers : >70%, >30 Layers : <5%
Thomas Swan Advanced Materials	Elicarb® Graphene	Graphene powder	few-layer graphene flakes with an average of 5-7 layers.
		Graphene Dispersion	A water/surfactant dispersed GNP at 1g/l.
ACS Material	Graphene Series	Single Layer Graphene, surface area (g/m^2): 400~1000; Electrical resistivity (Ω·cm) ≤ 0.30	
		Nitrogen-doped Graphene 1-5 atomic layer , Lateral size : 0.5-5 μm; surface area (g/m^2): 500~700 ; Conductivity (S/m) >1000	
		Industrial-Quality Graphene, Thickness (nm) ≤ 3.0; surface area (g/m^2): ~600; Electrical resistivity (Ω.cm) ≤ 0.30	

		Carboxyl Graphene, Diameter 1~5 µm, thickness 0.8~1.2 nm, Carboxy ratio ~ 5.0%, Purity ~ 99%
		Carboxyl Graphene, Carboxyl Graphene Water Dispersion Diameter 1~5 µm, thickness 0.8~1.2 nm, Carboxy ratio ~ 5.0% Purity ~ 99%
		Graphene Oxide Diameter 1~5 µm, thickness 0.8~1.2 nm, single layer ratio ~ 99%. Purity~ 99%. Diameter 1~15 µm, thickness 0.8-1.2 nm
		Graphene Oxide, High Surface Area Graphene Oxide Diameter 1~5 µm, thickness 0.8~1.2 nm, single layer ratio ~ 99%. Purity~ 99%.
		Single Layer, Oxide Ethanol Dispersion, Flake size: 0.5-2.0 µm; thickness: 0.6-1.2 nm; Single-layer Ratio: >80%
ACS Material	Graphene Series	Single Layer Graphene Oxide Water Dispersion (1)10 mg/ml, 100 ml (1 g), Flake size: 0.5-2.0 µm; Thickness: 0.6-1.2 nm; Single-layer Ratio: >80% (2) 10 mg/ml, 100 ml (0.5 g), Flake size: 500 nm; Thickness: 0.6-1.2 nm; Single-layer Ratio: >80%
		Diameter: ~5 µm; Thickness: 2-10 nm; surface area (g/m^2): 20-40 , Conductivity: 80000 S/m
		Graphene Film-Super Paper, Diameter: 40 mm, thickness: 20 µm, Conductivity: 2000 S/m
		Graphene Oxide Film, Diameter: 40 mm, thickness: 20 µm; Non-conductive, 8x10^{-2} S/m
		Aminated Graphene, Conductivity: 6.36 S/m
	CVD Graphene	Trivial Transfer Graphene, Predominantly single-layer graphene; Transparency: >95%
		3D Graphene Foam, Sheet Resistance: <600 Ω/sq
		Graphene on Copper Foil, Sheet Resistance: <600 Ω/sq
		Graphene on Si 1) Super large size graphene on copper foil up to 30 cm x 20 cm; 2) Double or multi-layer graphene; 3) transferred onto silicon substrate; Sheet Resistance: <600 Ω/sq; Transparency: >95%
		Graphene on SiO_2 1) Super large size graphene on copper foil up to 30 cm x 20 cm; 2) Double or multi-layer graphene; 3) transferred onto silicon dioxide substrate; Sheet Resistance: <600 Ω/sq;

		Transparency: >95%
		Graphene on PET 1) Super large size graphene on copper foil up to 30 cm x 20 cm; 2) Double or multi-layer graphene; 3) Graphene transferred onto PET substrate
		Graphene on Plastic, Graphene transferred to Plastic substrate (a polymer mainly containing PET <10%)
		Graphene on Quartz, Single Layer Graphene on Quartz Substrate; Sheet Resistance: <600 Ω/sq; Transparency: >95%
		Multi-layer , Predominantly Double- or Multi-Layer Graphene; Sheet Resistance: <600 Ω/sq; Transparency: >95%
		PMMA-coated , Pretreated Graphene-PMMA Coated; Sheet Resistance: <600 Ω/sq; Transparency: >95%
	Graphene Quantum Dots	Aminated Graphene Quantum Dots, Solution, Colorless solution; PL peak: 440 nm; Particle Size: ＜5 nm; Concentration: 1 mg/ml (available up to 20 mg/ml);Solution: Water
		Blue Luminescent Quantum Dots, Quantum Dots Size 15 <nm, Thickness 0.5 ~ 2 nm, Purity ~ 80%, concentration 1mg/ml.
		Carboxylated Graphene Quantum Dots, Solution, Colorless solution; PL peak: 487 nm; Particle Size: ＜10 nm; Concentration: 1 mg/ml (available up to 20 mg/ml);Solution: Water
		Carboxylated Graphene Quantum Dots, pale yellow powder; PL peak: 487 nm; Particle Size: ＜10 nm.
		Chlorine Functionalized Graphene Quantum Dots, Solution, Colorless solution; PL peak: 452 nm; Particle Size: ＜6 nm. Concentration: 1 mg/ml (available up to 2 mg/ml), Solution: Water, Containing a little ethylene glycol
		Green Graphene Quantum Dots, Solution, Colorless solution; PL peak: 530 nm; Particle Size: ＜6 nm. Concentration: 1 mg/ml (available up to 2 mg/ml), Solution: Water, Containing a little DMF
		Hydroxylated Graphene Quantum Dots, Solution, Colorless solution; PL peak: 375 nm; Particle Size: ＜6 nm. Concentration: 1 mg/ml (available up to 2 mg/ml), Solution: Mixture of water and ethylene glycol
XG Science	xGnP bulk dry powder	Grade C, an average particle diameter of less than 2 microns. Average surface areas are 300, 500 and 750 g/m^2.
		Grade H, a typical surface area of 60 to 80 g/m^2, available with average particle diameters of 5, 15 or 25 μm.

		Grade M, ~ 6 to 8 nm , surface area of 120 to 150 g/m², available with average particle diameters of 5, 15 or 25 µm.
	xGnP dispersions	Aqueous: xGnP® Graphene Nanoplatelets can be dispersed into water with probe sonication or high shear mixing.
		Organic solvents, Suggested solvents include NMP, DMF, THF, toluene, ethyl acetate, isopropanol, ethanol, acetone, methyl ethyl ketone (MEK) and chloroform, 2 amino-butane and other polar solvents.
		Resins and custom
Advanced Graphene Products	MONOLAYER Graphene MONOLAYER Graphene	HSMG™ on PMMA. Transparent film, Optical transmittance at 550 nm: >97%; Coverage: >95%; 1 layer; Thickness (theoretical): ~0.345 nm; sheet resistance: 220-800 Ohm/sq; Grain size: Up to 1 mm
		HSMG™ monolayer on Si, Substrate: Si(B) (111) type p; Thickness 300 µm ; Single side polished; Res: 9-12 ohm/cm
	MULTILAYER Graphene	HSMG™ on PMMA., Transparent film, Optical transmittance at 550 nm: >85%; Coverage: >95%; 3-5 layers; sheet resistance < 800 Ohm/sq; Grain size: Up to 1 mm
		HSMG™ monolayer on Si, Substrate: Si(B) (111) type p; Thickness 300 µm ; Single side polished; Res: 9-12 ohm/cm
NanoXplore	NXE-Graphene	Grade A: Purity: 96% by weight, Average Specific surface area : 25-30 g/m², 4-5 layers; Average sheet diameter : 5-20 µm. Highly OH edge functionalized
		Grade B: Purity: 96% Average Specific surface area : 10-15 g/m², 2-3 layers; Average sheet diameter : 0.5-5 µm. Highly OH edge functionalized
		Grade C: Purity: 96% Average Specific surface area : 200 g/m², 4-5 layers; Average sheet diameter : 5-20 µm,
		Grade D Purity: 96% Average Specific surface area : 10-15 g/m², 2-3 layers; Average sheet diameter :0.5-5 µm,
	NXE-Graphite Graphene – Composite	Grade E Purity: 96% by weight, Average Specific surface area :7-9 g/m², 5 -20 µm graphene sheets mixed with large natural graphite flakes
	NXE-Graphene Partially Oxidized	Grade F1: Purity: 96% by weight, Average Specific surface area : 100 g/m², 2-3 layers, 200-500 nm, C content: 75% (with 20% Oxygen), Impurity: 2 wt.%, Humidity: 2 wt.%, Low defect density
	NXE-GO	Grade F2 Purity: 96% by weight, Average Specific surface area : 100 g/m², 2-3 layers, 100-200 nm, C content: 60% (with 30% Oxygen),

RS MINES	Reduced GO (RSrGO) Paste	highly oxidised, highly conductive reduced graphene oxide paste, multiple uses including the enhancement of energy storage devices, conductive additive for polymers, and of course to make single to few layer graphene.
Graphenea	Suspended Monolayer Graphene	on Cavities, Substrate size up to 1.5 x 1.5 cm, Substrate withstand 450 ºC Temperature, Cavity size up to 30 µm, Minimum cavity depth: 500 nm, Film, transparent; transparency >97%, 1 layer, thickness :0.345 nm, Grain size: Up to 10 µm
	Monolayer Graphene	on SiO_2/Si or Cu or SiO_2/S or PET or Quartz Film, Transparency: >97 %, Coverage: >95%, Thickness (theoretical): 0.345 nm, Grain size: Up to 10 µm
	Bilayer Graphene	on SiO_2/S, Transparency >94%, Appearance (Form): Film, Coverage >95%, 2 layer, Thickness : 0.69 nm, Grain size: Up to 10 µm
	Trilayer Graphene	on SiO_2/S, Transparency >92%, Appearance (Form): Film, Coverage >95%, 3 layer, Thickness : 1.035 nm, Grain size: Up to 10 µm
	Suspended Monolayer Graphene	on TEM Grids (Quantifoil Gold) , Film, Transparency: >97 %, Coverage: >95%, Thickness : 0.345 nm, Grain size: Up to 10 µm
	Graphene Oxide	Form: Dispersion of graphene oxide sheets, Sheet dimension: Variable, Colour: Yellow-brown, Odour: Odourless Dispersibility: Polar solvents, Solvent: Water, pH: 2,2 - 2,5 Concentration: 4 mg/mL, Monolayer content (measured in 0.5 mg/mL): >95% (*)
		Form: Dispersion of graphene oxide sheets, Solvent: Water, Concentration: 0.5 mg/mL, Monolayer content
	Reduced Graphene Oxide	Form: Powder, Sheet dimension: Variable, Colour: Black, Odour: Odourless, Solubility: Insoluble Dispersability: It can be dispersed at low concentrations (<0.1 mg/mL) in NMP, DMSO, DMF
	GO Film	Diameter: 4 cm, Thickness: 12-15 µm, Non-conductive
Angstron Materials	Graphene and GO Dispersions	N002-PS-0.5 Graphene Oxide Solution Water Content (percent): ≥ 99.50, Average Z Dimension (nm): 1.0 – 1.2, Average X & Y Dimensions (um): 0.554
		N002-PS-1.0 Graphene Oxide Solution Average Z Dimension: 1-1.2 nm , (Single Layer GO), Average X-Y Dimension: ~ 500 nm
	Graphene and GO Powder	N002-PDE Graphene Oxide Powder Few Layer Graphene Oxide, 2-3 nm , lateral size ≤ 7 µm, Specific Surface

		Area (g/m²): ≥ 400
		N008-P-40 Polar Graphene Powder Average Z Dimension (nm): 50 – 100, Average X & Y Dimensions (um): ≤ 10, Specific Surface Area (g/m²): 20-40
		N008-P-10 Polar Graphene Powder Average Z Dimension (nm): 50 – 100, Average X & Y Dimensions (um): ≤ 7, Specific Surface Area (g/m²): ≤ 40
		N008-N Pristine Graphene Powder Average Z Dimension (nm): 50 – 100, Average X & Y Dimension (um): 5, Specific Surface Area (g/m²): ≤ 30
		N006-P Polar Graphene Powder Average Z Dimension (nm): 10 – 20, Average X & Y Dimensions (um): 5, Specific Surface Area (m²/g): ≥ 15
		N002-PDR Few Layer Graphene Powder Less than 3 layers, Average X & Y Dimensions (um): ≤ 10, Specific Surface Area (m²/g): 400 – 800

Summary of processing parameters

Table S3. Processing parameters used in Three Roll Mill processing.

Processing Parameters	Levels									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
I. Shear Rate	5µm, 30 rpm	5 µm, 60 rpm	5 µm, 90 rpm	5 µm, 150 rpm	5µm, 200 rpm	120/40µm, 200 rpm	60/20 µm, 200 rpm	30/10 µm, 200 rpm	15/5 µm, 200 rpm	5N/mm 200 rpm
II. Filler concentration	1.0 wt.%	2.0 wt.%	3.0 wt.%	4.0 wt.%	5.0 wt.%	-	-	-	-	-
III. Temperature	25 °C	30 °C	35 °C	40 °C	-	-	-	-	-	-
IV. Number of cycles	1	2	3	4	5	6	7	8	9	10
V. Direct (D) Vs Masterbatch (M) + Dilution (D)	D	M+D	-	-	-	-	-	-	-	-

Table S4 Experimental trials of different processing parameters of TRM.

		I										II					III				IV										V	
		1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	1	2	3	4	1	2	3	4	5	6	7	8	9	10	1	2
I	1											X	X	X	X	X	X				X	X									X /O	
	2											X	X	X	X	X	X						X	X							X /O	
	3											X	X	X	X	X	X								X	X					X /O	
	4											X	X	X	X	X	X										X	X			X /O	
	5											X	X	X	X	X	X												X	X	X /O	
	6											X	X	X	X	X	X				O/T										X /O	
	7											X	X	X	X	X	X					O/T									X /O	
	8											X	X	X	X	X	X														X /O	
	9											X	X	X	X	X	X														X	
	10											X	X	X	X	X	X						O/T	O/T	O/T	O/T	O/T	O/T			X	
II	1						O	O			O						X /O				X /O	X /O	X /O	X /O	X /O	X /O	X /O	X /O	X	X	X /O	
	2						O	O			O						X /O				X /O	X /O	X /O	X /O	X /O	X /O	X /O	X /O	X	X	X /O	
	3						O/T	O/T			O/T						X /O	T	T	T	X /O	X /O	X /O	X /O	X /O	X /O	X /O	X /O	X	X	X /O	
	4						O/T	O/T			O/T						X /O	T	T	T	X /O	X /O	X /O	X /O	X /O	X /O	X /O	X /O	X	X	X /O	
	5						O/T	O/T			O/T						X /O	T	T	T	X /O	X /O	X /O	X /O	X /O	X /O	X /O	X /O	X	X	X /O	O
III	1						O/T	O/T			O/T	X /O	X /O	O/T	O/T	O/T					O/T	O/T	O/T	O/T	O/T	O/T	O/T	O/T			O/T	
	2						O/T	O/T			O/T			O/T	O/T	O/T					O/T	O/T	O/T	O/T	O/T	O/T	O/T	O/T			O/T	
	3						O/T	O/T			O/T			O/T	O/T	O/T					O/T	O/T	O/T	O/T	O/T	O/T	O/T	O/T			O/T	
	4						O/T	O/T			O/T			O/T	O/T	O/T					O/T	O/T	O/T	O/T	O/T	O/T	O/T	O/T			O/T	
IV	1	X					O/T					X /O	X /O	X /O/T	X/O/T	X/O/T	X /O	O/T	O/T	O/T											X/O/T	
	2	X						O/T				X /O	X /O	X /O/T	X/O/T	X/O/T	X /O	O/T	O/T	O/T											X/O/T	
	3		X								O/T	X /O	X /O	X /O/T	X/O/T	X/O/T	X /O	O/T	O/T	O/T											X/O/T	
	4		X								O/T	X /O	X /O	X /O/T	X/O/T	X/O/T	X /O	O/T	O/T	O/T											X/O/T	
	5			X							O/T	X /O	X /O	X /O/T	X/O/T	X/O/T	X /O	O/T	O/T	O/T											X/O/T	
	6			X							O/T	X /O	X /O	X /O/T	X/O/T	X/O/T	X /O	O/T	O/T	O/T											X/O/T	
	7				X						O/T	X /O	X /O	X /O/T	X/O/T	X/O/T	X /O	O/T	O/T	O/T											X/O/T	
	8				X						O/T	X /O	X /O	X /O/T	X/O/T	X/O/T	X /O	O/T	O/T	O/T											X/O/T	
	9					X						X	X	X	X	X	X														X	
	10					X						X	X	X	X	X	X														X	
V	1	X	X	X	X	X	X	X	X	X	X	X /O	X /O	X /O	X /O	X /O	X/O	X/O	X/O	X/O	X/O	X/O	X/O	X/O	X/O	X/O	X/O	X/O	X	X		
	2									O	O					O/T	O/T	O/T	O/T	O/T												

X-Process I, O- process II, T-Temperature Controlled samples, using Process II.

References

1. Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 2nd ed; A Wiley-Interscience Publication: New York, 1967.
2. Cheng, C.-H.; Lin, H.-H. Measurement of Surface Tension of Epoxy Resins used in Dispensing Process for Manufacturing Thin Film Transistor-liquid Crystal Displays. IEEE Transcation on Adavanced Packaing **2008**, 31(1), 100-106.
3. Khan, U.; O'neill, A.; Porwal, H.; May, P.; Nawaz, K.; Coleman, J. N., Size Selection of Dispersed, Exfoliated Graphene Flakes by Controlled Centrifugation. *Carbon* **2012,** *50* (2), 470-475.
4. Khan, U.; Porwal, H.; O'neill, A.; Nawaz, K.; May, P.; Coleman, J. N., Solvent-exfoliated Graphene at Extremely High Concentration. *Langmuir* **2011,** *27* (15), 9077-9082.
5. Lu, J.; Yang, J.-X.; Wang, J.; Lim, A.; Wang, S.; Loh, K. P., One-pot Synthesis of Fluorescent Carbon Nanoribbons, Nanoparticles, and Graphene by the Exfoliation of Graphite in Ionic Liquids. *ACS Nano* **2009,** *3* (8), 2367-2375.
6. Reina, A.; Jia, X.; Ho, J.; Nezich, D.; Son, H.; Bulovic, V.; Dresselhaus, M. S.; Kong, J., Large Area, Few-layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Lett.* **2008,** *9* (1), 30-35.
7. Dhakate, S.; Chauhan, N.; Sharma, S.; Tawale, J.; Singh, S.; Sahare, P.; Mathur, R., An Approach to Produce Single and Double Layer Graphene from Re-exfoliation of Expanded Graphite. *Carbon* **2011,** *49* (6), 1946-1954.
8. Xia, Z. Y.; Pezzini, S.; Treossi, E.; Giambastiani, G.; Corticelli, F.; Morandi, V.; Zanelli, A.; Bellani, V.; Palermo, V., The Exfoliation of Graphene in Liquids by Electrochemical, Chemical, and Sonication-assisted Techniques: A Nanoscale Study. *Adv. Funct. Mater.* **2013,** *23* (37), 4684-4693.
9. Liu, N.; Luo, F.; Wu, H.; Liu, Y.; Zhang, C.; Chen, J., One Step Ionic Liquid Assisted Electrochemical Synthesis of Ionic Liquid Functionalized Graphene Sheets Directly from Graphite. *Adv. Funct. Mater.* **2008,** *18* (10), 1518-1525.
10. Wang, J.; Manga, K. K.; Bao, Q.; Loh, K. P., High-yield Synthesis of Few-layer Graphene Flakes through Electrochemical Expansion of Graphite in Propylene Carbonate Electrolyte. *JACS* **2011,** *133* (23), 8888-8891.
11. Su, C.-Y.; Lu, A.-Y.; Xu, Y.; Chen, F.-R.; Khlobystov, A. N.; Li, L.-J., High-quality Thin Graphene Films from Fast Electrochemical Exfoliation. *ACS Nano* **2011,** *5* (3), 2332-2339.
12. Alanyalıoğlu, M.; Segura, J. J.; Oro-Sole, J.; Casan-Pastor, N., The Synthesis of Graphene Sheets with Controlled Thickness and Order Using Surfactant-assisted Electrochemical Processes. *Carbon* **2012,** *50* (1), 142-152.

13. Morales, G. M.; Schifani, P.; Ellis, G.; Ballesteros, C.; Martínez, G.; Barbero, C.; Salavagione, H. J., High-quality Few Layer Graphene Produced by Electrochemical Intercalation and Microwave-assisted Expansion of Graphite. *Carbon* **2011,** *49* (8), 2809-2816.

14. Zhao, J.; Pei, S.; Ren, W.; Gao, L.; Cheng, H.-M., Efficient Preparation of Large-area Graphene Oxide Sheets for Transparent Conductive Films. *ACS Nano* **2010,** *4* (9), 5245-5252.

15. Pan, S.; Aksay, I. A., Factors Controlling the Size of Graphene Oxide Sheets Produced via the Graphite Oxide Route. *ACS Nano* **2011,** *5* (5), 4073-4083.

16. Luo, Z.; Lu, Y.; Somers, L. A.; Johnson, A. C., High Yield Preparation of Macroscopic Graphene Oxide Membranes. *JACS* **2009,** *131* (3), 898-899.

17. Khan, U.; O'neill, A.; Lotya, M.; De, S.; Coleman, J. N., High-concentration Solvent Exfoliation of Graphene. *Small* **2010,** *6* (7), 864-871.

18. Green, A. A.; Hersam, M. C., Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation. *Nano Lett.* **2009,** *9* (12), 4031-4036.

19. Lotya, M.; Hernandez, Y.; King, P. J.; Smith, R. J.; Nicolosi, V.; Karlsson, L. S.; Blighe, F. M.; De, S.; Wang, Z.; Mcgovern, I., Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions. *JACS* **2009,** *131* (10), 3611-3620.

20. Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; Mcgovern, I.; Holland, B.; Byrne, M.; Gun'ko, Y. K., High-yield Production of Graphene by Liquid-Phase Exfoliation of Graphite. *Nat. Nanotechnol.* **2008,** *3* (9), 563-568.

21. Yi, M.; Shen, Z.; Zhang, X.; Ma, S., Achieving Concentrated Graphene Dispersions in Water/Acetone Mixtures by the Strategy of Tailoring Hansen Solubility Parameters. *J. Phys. D: Appl.Phys.* **2013,** *46* (2), 025301.

22. Zhao, W.; Fang, M.; Wu, F.; Wu, H.; Wang, L.; Chen, G., Preparation of Graphene by Exfoliation of Graphite Using Wet Ball Milling. *J. Mater. Chem.* **2010,** *20* (28), 5817-5819.

23. Zhao, W.; Wu, F.; Wu, H.; Chen, G., Preparation of Colloidal Dispersions of Graphene Sheets in Organic Solvents by Using Ball Milling. *J.Nanomater.* **2010,** 6.1-5

24. Wu, H.; Zhao, W.; Hu, H.; Chen, G., One-Step In Situ Ball Milling Synthesis of Polymer-Functionalized Graphene Nanocomposites. *J.Mater. Chem.* **2011,** *21* (24), 8626-8632.

25. Chen, J.; Duan, M.; Chen, G., Continuous Mechanical Exfoliation of Graphene Sheets via Three-Roll Mill. *J.Mater. Chem.* **2012,** *22* (37), 19625-19628.

26. Raza, M.; Westwood, A.; Brown, A.; Stirling, C., Texture, Transport and Mechanical Properties of Graphite Nanoplatelet/Silicone Composites Produced by Three Roll Mill. *Compos. Sci. Technol.* **2012,** *72* (3), 467-475.

27. Raza, M.; Westwood, A.; Stirling, C. Graphite Nanoplatelet/Silicone Composites for Thermal Interface Applications, International Symposium on Advanced Packaging Materials: Microtech (APM). IEEE, **2010**, 34-48.